

## Kinetic Studies of Catalytic Ozonation of Atrazine

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The aim of our work was to degrade atrazine by the ozone treatment of both a model and the original drinking water samples, using Pt-catalyst, and to evaluate the performance of this catalyst. The rate constant for the reaction of atrazine with ozone was determined in the model water sample. The activation energies and the reaction orders of ozone decomposition were determined in both the model and the drinking water samples. Ozone treatment using Pt-catalyst has some influence on the loss of atrazine in the sources of drinking water. The concentration of some metabolites in the model and drinking water was observed during ozone treatment. The toxicity of atrazine to crustacean *Daphnia magna* in the original drinking water and in the ozone treated water samples was also assessed.

### INTRODUCTION

Pesticide atrazine is the most commonly present pesticide in the drinking water in Slovenia.<sup>1,2</sup> The drinking water directive 98/83/EC<sup>3</sup> sets an allowed contaminant level of 0.1  $\mu\text{g L}^{-1}$  for a single pesticide, and 0.5  $\mu\text{g L}^{-1}$  for the total sum of pesticides. According to the previous studies, atrazine degradation by ozone, or coupled with hydrogen peroxide, may be achieved through various processes which include dealkylation of the amino groups, formation of amides, and hydroxylation (*via* deamination and/or dechlorination). Many authors<sup>4–7</sup> claimed that no ring opening occurs, and that cyanuric acid has been detected under certain conditions as the end product. Atrazine has been shown to undergo hydrolysis to hydroxyl atrazine in aqueous acidic and alkaline buffer solutions, while hydrolysis is very slow process at neutral pH.<sup>8</sup> Ozone reactions with organic pollutants in aqueous systems may occur following two courses: either direct at-

tack by molecular ozone *via* cycloaddition or the decomposition of ozone.<sup>9</sup>

Catalytic ozone treatment is a new technology which has been developed over recent years. Ni<sup>10</sup> discovered, that the reaction rate increased when Pb<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup>, Ti<sup>2+</sup> and Mn<sup>2+</sup> ions were applied in the oxidation of 2-dichlorophenol using ozone. Ma<sup>11</sup> showed that an inverse linear relationship exists between the dosed Mn<sup>2+</sup> concentration and the atrazine concentration monitored over a specific reaction time. Manganese catalyst decomposes in water which, consequently, increases Mn<sup>2+</sup> content in potable water and might affect the taste or even lead to digestion problems when drinking such water. Platinum is chemically inert and offers advantages over other metal catalysts.

Therefore, the aim of this article is to determine the kinetics of the atrazine degradation *via* ozone treatment using Pt catalyst. Two sets of experiments were carried

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out under the same reaction conditions: first using a model water sample and the second concerned an original potable water sample.

## METHODS

### Materials

Commercially – available atrazine (CIET): 2-chloro-4-ethylamino-6-isopropylamine-1,3,5-triazine, desethyl-atrazine (CIAT): 2-amino-4-chloro-6-isopropylamino-*s*-triazine, desisopropylatrazine (CEAT): 2-amino-4-chloro-6-ethylamino-*s*-triazine (98 %, purchased from Merck) and 2-methyl-2-propanol (*tert*-butyl alcohol, Merck) were used.

The model water sample was prepared by dissolving the appropriate concentration of atrazine in the distilled water.

The potable water sample was taken directly from a water well V2 with a depth of 24 m (Table I).

In some experiments Pt-catalysts (TiO<sub>2</sub> support, small sticks, Rosemount Analytical Division, Dohrmann, P/N 14-7687-0), which was previously preconditioned (washed with deionised water and dried at 50 °C), was added to the water solution of the atrazine prior to ozone treatment.

### Instrumentation

Water samples undergo a solid phase extraction (SPE) prior to their analysis by GC/MS. Solid phase extraction consists of the retention of atrazine (CIET), desethyl-atrazine (CIAT) and desisopropylatrazine (CEAT) in a solid phase and subsequent elution with an organic solvent. During SPE, 1000 mL of the drinking water (and 100 mL in case of using model water) is passed through cartridges containing a solid ENV (styrene divinyl benzene adsorption phase, Varian cartridges, 500 mg 6 mL<sup>-1</sup>). The cartridge was conditioned by rinsing twice with ethylacetate, followed by rinsing twice with methanol, and twice with deionised water. Pesticides were eluted by passing 5 mL of ethylacetate and methanol solution through the cartridge. The extracts were evaporated until obtaining an approximate volume of 0.5 mL using Supelco vacuum pumps. This extracts were analysed by GC/MS. Separation was performed on 30 m × 0.25 mm DB5-MS (J&W Scientific) column (Hewlett Packard 5890, type II instrument) using helium as the carrier gas. A split-splitless injection in the splitless mode was used and the temperature was programmed from 50 °C (initial time, 2 min) to 170 °C at a rate of 20 °C min<sup>-1</sup>, 170–195 °C at a rate of 1 °C min<sup>-1</sup>, 195–260 °C at a rate of 20 °C min<sup>-1</sup> and held at 260 °C for 5 min. The injector and mass spectrometer (Hewlett Packard 5972) temperatures were held at 280 °C. The electron impact energy was set at 70 eV. Limits of quantification were 0.05 µg L<sup>-1</sup>, for CIET, CIAT, and CEAT, each individually.

The concentration of anions in potable water was determined by Ion Chromatograph Dionex DX-100, in line with ISO 10304-2, pH was then determined electrochemically according to SIST ISO 10523.

Total organic carbon (TOC) and total nitrogen (TN) were determined with TOC-V<sub>CPN</sub>, TNM-1, Shimadzu, in line with ISO 8245 standard. Toxicity was determined following ISO 6341. The concentrations of Pt and Ti were determined by spectrometric measurements using ICP-MS Agilent 7500 c, in line with DIN 38406-29.

## OZONE TREATMENT AND KINETIC STUDIES

### Oxidation Using Ozone

Ozone was generated from dry oxygen using a Wedeco Ozomatic Modular 4HC LAB ozone generator. The inlet oxygen pressure was 0.5 bar, gas flow was set to 15, 55 and 115 L h<sup>-1</sup>, respectively. Ozone production rates of 17.2, 4.1 and 2.6 mg of ozone per m<sup>3</sup> of gas, respectively, were applied. The ozone concentration from the output of the ozone generator was determined by passing the ozone – oxygen mixture through two tandem reactors, filled with KI (10 g L<sup>-1</sup>) dissolved in a phosphate buffer (14.2 g L<sup>-1</sup> Na<sub>2</sub>HPO<sub>4</sub> and 10 g L<sup>-1</sup> KH<sub>2</sub>PO<sub>4</sub>, pH was 6.8 ± 0.2). The flow rate of gas was controlled by a valve, through which different ozone dosages were added to the KI solution. The KI solution was, subsequently, titrated with 0.2 mol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> according to the standard methods.

A generator was connected to the reactor ( $V = 1$  L) for the kinetic measurements, filled with an atrazine-containing water sample. Ozone was dissolved in the solution by Assistant glass frit, and IKA magnetic stirrer was used. The residual ozone, which left the first reactor, was trapped in KI solution in the second 0.5 L reactor. The residual ozone concentration was determined by using indigo method on Hach Dr/890 photometer.

### Determination of the Reaction Rate of CIET Loss

Rate constant for the direct reaction of ozone with atrazine was measured in water in the presence of a hydroxyl radical scavenger in order to minimize interfering radical chain reactions. Model water samples were prepared by spiking 0.029 mmol L<sup>-1</sup> atrazine in distilled water. Samples were taken every 5 minutes up to 20 minutes. In the second series the samples were spiked with 52.4 mmol L<sup>-1</sup> tertiary butanol (*tert*-BuOH). The gas flow was set at 15 L h<sup>-1</sup>. The water samples ( $V = 1$  L) were preserved by adding 5 mL 0.2 mol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> immediately after the end of ozone treatment. Prior to ozone treatment, Pt catalyst was added into the samples.

### Determination of Activation Energy

The rate constants for the reaction of atrazine with ozone were determined in the model water. pH value was adjusted to 5.2. The concentrations of CIET were measured during the ozone treatment. The concentration of CIET was plotted *versus* time. Model water with  $0.68 \mu\text{mol L}^{-1}$  atrazine was treated using ozone at 6 different temperatures: 5, 10, 15, 22, 30 and  $40 \text{ }^{\circ}\text{C}$ . The water samples were preserved by adding  $5 \text{ mL } 0.2 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$  to  $1 \text{ L}$  of water sample immediately after the end of ozone treatment. Prior to ozone treatment, Pt catalyst was added into the samples.

### Determination of the Order of Reaction with Respect to Ozone

Four sets of experiments were done under the same reaction conditions: the first set was carried out using model water prepared by spiking atrazine in distilled water, the second used the same samples but contained the addition of Pt-catalyst, the third set consisted of the potable water, extracted from a commercial well, contaminated with atrazine, and the fourth set was similar to the third set but had the addition of Pt-catalyst.

The samples were treated by ozone at 3 different gas-flows  $15, 55$  and  $115 \text{ L h}^{-1}$ . Samples were taken after 2, 5, 10, 15 and 20 min of ozone treatment. The water samples were preserved by adding  $5 \text{ mL } 0.2 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$  to  $1 \text{ L}$  of water sample immediately after the end of ozone treatment.

**Toxicity test.** – Model water was spiked with  $4.6 \mu\text{mol L}^{-1}$  CIET, then oxidized by ozone for 30 and 60 minutes, at gas flow  $15 \text{ L h}^{-1}$  and at  $22 \text{ }^{\circ}\text{C}$ . The toxicity of pesticides in water samples to crustacean *Daphnia magna* was examined.

## RESULTS AND DISCUSSION

Experiments were performed at room temperature in the range between  $20$  and  $24 \text{ }^{\circ}\text{C}$ . When the influence of temperature on the reactions was considered, the temperature was changed from  $5$  to  $40 \text{ }^{\circ}\text{C}$ . The original temperature of water in the well ranged from  $12$  to  $15 \text{ }^{\circ}\text{C}$ .

### Determination of the Reaction Rate Constants for Reaction of Atrazine with Ozone

An organic substrate monitoring method<sup>12</sup> was applied in order to determine the reaction rate of CIET loss during the reaction with ozone molecule. Using *tert*-BuOH as radical scavenger ( $52.4 \text{ mmol L}^{-1}$ ), we investigated as to whether ozone treatment at acidic pH is the subject of direct oxidation by the ozone molecule or a radical mechanism by secondary oxidants, such as hydroxyl radicals. After adding *tert*-butanol, the decrease in ozone and concentrations of CIET were measured.

TABLE I. Original drinking water analysis

Parameter	Measurements
Temperature/ $^{\circ}\text{C}$	20
pH-value	7.58–7.60
Cl/ $\text{mg L}^{-1}$	35
$\text{NO}_3/\text{mg L}^{-1}$	< 0.1
$\text{SO}_4/\text{mg L}^{-1}$	2.75
TOC/ $\text{mg L}^{-1}$ (as C)	4.671
TN/ $\text{mg L}^{-1}$ (as N)	2.891
CIET/ $\mu\text{g L}^{-1}$	0.15
CIAT/ $\mu\text{g L}^{-1}$	0.21
CEAT/ $\mu\text{g L}^{-1}$	< 0.05

Equations (1) and (2) were applied to determine the reaction rate of CIET loss.

$$\ln(\gamma_0 \gamma_t^{-1}) = k_{\text{exp}} t \quad (1)$$

$$k_{\text{CIET}} = k_{\text{exp}} \gamma_{\text{O}_3\text{avg}}^{-1} \quad (2)$$

where  $\gamma_0$  is the initial mass concentration of CIET (in  $\text{mg L}^{-1}$ ),  $\gamma_t$  is the mass concentration of the organic compound (in  $\text{mg L}^{-1}$ ) at time  $t$ ,  $k_{\text{exp}}$  is the experimental rate constant of consumption of CIET (in  $\text{min}^{-1}$ ),  $t$  is the experimental time (in min),  $\gamma_{\text{O}_3\text{avg}}$  is the average of the initial and final ozone concentrations (in  $\text{mg L}^{-1}$ ), and  $k_{\text{CIET}}$  is the reaction rate of CIET loss (in  $\text{s}^{-1} \text{ L mol}^{-1}$ ).

The calculated rate constants for CIET loss by ozone treatment were  $9.2 \text{ s}^{-1} \text{ L mol}^{-1}$  and  $9.7 \text{ s}^{-1} \text{ L mol}^{-1}$  in case of ozone treatment with Pt-catalyst. The rate constants for CIET loss were  $10.4 \text{ s}^{-1} \text{ L mol}^{-1}$  and  $11.1 \text{ s}^{-1} \text{ L mol}^{-1}$  for ozone treatment and ozone treatment with Pt-catalyst, respectively, without *tert*-BuOH applied. A little increase of the reaction rate was observed in experiments without *tert*-BuOH. This means that the radical scavenger *tert*-BuOH has little influence on the reaction rate of the ozone treatment at  $\text{pH} = 5.2$ . Thus it can be concluded that ozone treatment in the acidic solution is subjected to direct oxidation by the ozone.

The determined rate constant for CIET loss is higher than reported elsewhere ( $6.0 \pm 0.3 \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$ )<sup>12</sup> and this can be connected to the higher temperature and to the concentration of CIET in the solution. It can not be excluded that ozone treatment at  $\text{pH} = 5.2$  is initiated by small concentrations of hydroxyl radicals. However, in our research we confirmed that the ozone reacts directly with atrazine.

### Determination of Activation Energy and the Reaction Order with Respect to Atrazine

As discussed above, ozone reacts with CIET directly at experimental  $\text{pH} = 5.2$ . Therefore an equation for CIET

disappearance rate can be written in the following form, as applied in literature:<sup>13</sup>

$$-d\gamma \, dt^{-1} = A_0 e^{(-E_a/RT)} \gamma^{n_{\text{CIET}}} \gamma_{\text{O}_3}^{n_{\text{O}_3}} \quad (3)$$

where  $\gamma$  is CIET mass concentration (in mg L<sup>-1</sup>),  $\gamma_{\text{O}_3}$  is the ozone mass concentration (in mg L<sup>-1</sup>),  $n_{\text{CIET}}$  is the reaction order with respect to atrazine,  $n_{\text{O}_3}$  is the reaction rate with respect to ozone,  $E_a$  is the activation energy for the reaction,  $R$  is the ideal gas constant (in J mol<sup>-1</sup> K<sup>-1</sup>), and  $T$  is the temperature (in K).

Since the experiments were carried out at a constant partial pressure of ozone, Eq. (3) can be further simplified to Eqs. (4) and (5):

$$-d\gamma \, dt^{-1} = k^* \gamma^{n_{\text{CIET}}} \gamma_{\text{O}_3}^{n_{\text{O}_3}}, \text{ and } k^* = A_0 e^{(-E_a/RT)} \quad (4)$$

$$-d\gamma \, dt^{-1} = k \gamma^{n_{\text{CIET}}}, \text{ and } k = k^* \gamma_{\text{O}_3}^{n_{\text{O}_3}} \quad (5)$$

where the apparent rate coefficient  $k$  (in min<sup>-1</sup>) stands for the product of the rate constant and the ozone concentration to the order  $n$ , and where  $\gamma$  is the mass concentration of CIET (in mg L<sup>-1</sup>),  $\gamma_{\text{O}_3}$  is the mass concentration of ozone (in mg L<sup>-1</sup>),  $n_{\text{CIET}}$  is the reaction order with respect to atrazine, and  $n_{\text{O}_3}$  is the reaction rate with respect to ozone.

Reaction with respect to atrazine was determined as the first order, therefore, Eq. (4) can be simplified to Eq. (5). It was assumed that the concentration of ozone to the order  $n$  is constant. The integrated form of CIET disappearance *vs.* time is plotted in Figure 1. The CIET disappearance rate is a first – order reaction with respect to the organic substrate in the acidic region which can be assumed from the straight lines in Figures 1 and 2.

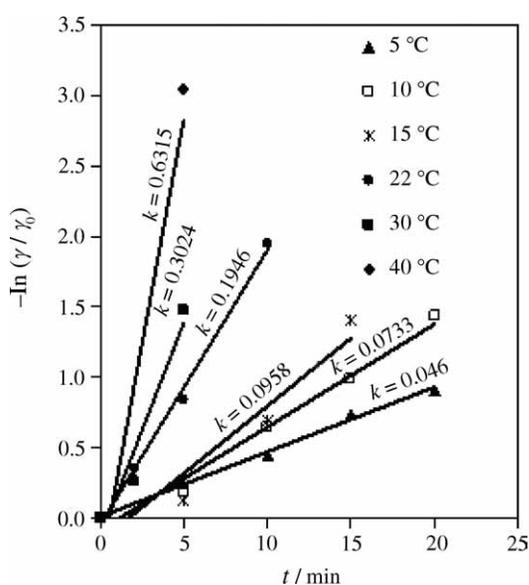


Figure 1. Kinetics of CIET removal by the ozone treatment of water samples at different temperatures, 0.5 bar pressure and gas flow of 15 L h<sup>-1</sup>.

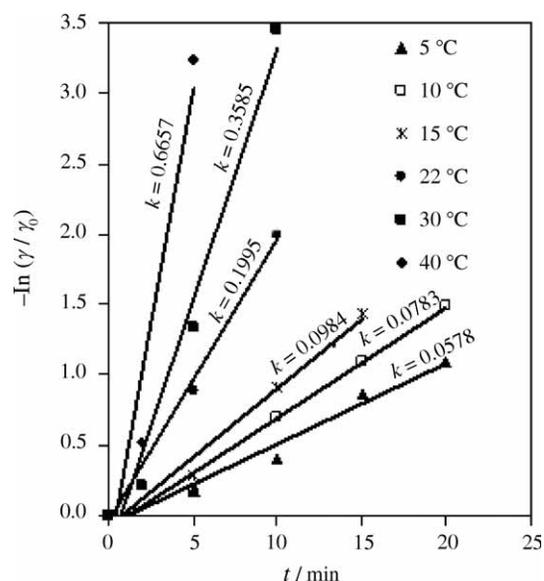


Figure 2. Kinetics of CIET removal by the catalytic ozone treatment of the water samples at different temperatures, 0.5 bar pressure and gas flow of 15 L h<sup>-1</sup>.

The activation energy of the reaction between ozone and atrazine was calculated from Arrhenius plot, at varying temperatures from 5 to 40 °C (Table II). The activation energy for CIET degradation was 53.8 kJ mol<sup>-1</sup> in the ozone treated sample and decreased to 52.3 kJ mol<sup>-1</sup> in the sample treated by ozone with Pt-catalyst. In the literature<sup>7,14</sup> a little lower activation energy values were found within a range between 35 and 50 kJ mol<sup>-1</sup>. These activation energies were determined for typically molecular ozone reactions observed between 5 and 20 °C and do show some agreements with our calculated values. The constant  $A_0$ , was calculated at  $5.9 \times 10^8$  L g<sup>-1</sup> min<sup>-1</sup> by ozone treatment (Table II), and at  $3.6 \times 10^8$  L g<sup>-1</sup> min<sup>-1</sup> by catalytic ozone treatment.

Since the experiments were performed under three different ozone partial pressures, the order of the reac-

TABLE II. Activation energy determination by catalytic ozone treatment (a) and ozone treatment (b)

$\theta/^\circ\text{C}$	$(T/\text{K})^{-1}$	$k/\text{min}^{-1(\text{a})}$	$\ln k$	$k/\text{min}^{-1(\text{b})}$	$\ln k$
5	0.0036	-0.0578	-2.850	-0.046	-3.079
10	0.0035	-0.0783	-2.547	-0.0733	-2.613
15	0.0035	-0.0984	-2.319	-0.0958	-2.345
30	0.0033	-0.3585	-1.026	-0.3024	-1.196
22	0.0034	-0.1995	-1.612	-0.1946	-1.637
40	0.0032	-0.6657	-0.407	-0.6315	-0.460
Calculated values					
$k^*/\text{min}^{-1}$		6296 <sup>(a)</sup>		6468 <sup>(b)</sup>	
$E_a/\text{kJ mol}^{-1}$		52.3 <sup>(a)</sup>		53.8 <sup>(b)</sup>	
$A_0/\text{L g}^{-1} \text{min}^{-1}$		$5.9 \times 10^8$ <sup>(a)</sup>		$3.6 \times 10^8$ <sup>(b)</sup>	

tion with respect to ozone by plotting  $\ln k$  vs.  $\ln \gamma_{O_3}$  can be estimated. Tables III to VI represent kinetic studies for different gas flows and a comparison between the kinetics of ozone treatment and catalytic ozone treatment. We discovered that the catalyst had some effect on reaction rate, because the reaction was faster during catalytic ozone treatment than during ozone treatment without Pt-catalyst. From Table IV it is obvious that the kinetic constants (using ozone treatment and catalytic ozone treatment) with respect to atrazine, hardly differ.

TABLE III. CIET mass concentrations (in  $\mu\text{g L}^{-1}$ ) dependence on ozone flows ( $Q$ ) at 22 °C, in the original water samples during ozone treatment (a) and catalytic ozone treatment (b)

$t/\text{min}$	$Q / \text{L h}^{-1}$					
	15 <sup>(a)</sup>	55 <sup>(a)</sup>	105 <sup>(a)</sup>	15 <sup>(b)</sup>	55 <sup>(b)</sup>	105 <sup>(b)</sup>
0	126	126	126	126	126	126
2	97	95	126	101	123	120
5	29	70	98	33	88	98
10	5	18	33	4	4	31
15		4	7		1	12
20			2			2

TABLE IV. Determination of the order of reaction with respect to atrazine in the original water sample at 22 °C using different gas flows ( $Q$ ) during ozone treatment (a) and catalytic ozone treatment (b)

$Q / \text{L h}^{-1}$	15 <sup>(a)</sup>	55 <sup>(a)</sup>	105 <sup>(a)</sup>	15 <sup>(b)</sup>	55 <sup>(b)</sup>	105 <sup>(b)</sup>
$k/\text{min}^{-1}$	0.336	0.232	0.197	0.359	0.255	0.206
$\ln k$	0.336	0.232	0.197	0.359	0.255	0.206
$\gamma_{O_3}/\text{mg L}^{-1}$	4.11	0.60	0.29	4.11	0.60	0.29
$\ln \gamma_{O_3}$	1.413	-0.511	-1.238	1.413	-0.511	-1.238
$n$	0.200			0.203		

From Table IV, the resultant order of reaction with respect to atrazine can be considered as 0.2 at ozone treatment and 0.203 at catalytic ozone treatment. It is obvious that there is no difference between ozone treatment with or without the catalyst, regarding the original water sample.

#### Determination of the Reaction Order with Respect to Ozone in Drinking Water

The concentration of CIET in drinking water was  $0.15 \mu\text{g L}^{-1}$ . The gas flows by ozone treatment were set at 15, 55 and  $115 \text{ L h}^{-1}$ . The measurements of CIET concentrations at ozone treatment are collected in Table V. As illustrated in Table VI, the reaction order with respect to ozone was 0.269 and for the ozone treatment with Pt-catalyst 0.284. Consequently, a slightly higher constant

rate was observed in the original drinking water sample compared to the model water. The reaction rate of CIET loss ( $k$ ) in drinking water (Table VI) was 27 % higher when catalyst was used, while it was only 5.6 % higher in the model water samples. This means that in the model water, the reaction rates were 2.6 times higher than in the drinking water when the catalytic ozone treatment was used and 3.3 times higher when the ozone treatment was used. The slower degradation of CIET in drinking water is due to high contents of carbonates and hydro-carbonates, which are the OH-radical scavengers.<sup>15</sup> Carbonate is a stronger radical scavenger than bicarbonate due to its higher reaction rate constant with hydroxyl radicals. Under neutral pH conditions, the inorganic carbon exists mainly in the form of bicarbonate, which is present in the surface and ground waters. Bicarbonate ion is reported to take part in reactions with hydroxyl radicals in competition with relatively lower rate constants due to scavenged hydroxyl radicals and, thereby, quenching the radical type chain reaction.<sup>16</sup> In addition, drinking water contains from 1 to  $2 \text{ mg L}^{-1}$  of total organic carbon (TOC), which can also play the role of scavenger or promoter during ozone decomposition.<sup>17</sup> Therefore, the values of  $k$  in drinking water are higher by 27 % using catalytic ozone treatment. Natural organic material, such as humic-acids or amino acids might have a significant effect on the kinetics of CIET decomposition.<sup>18</sup>

Therefore, we established that first order reactions could be applied for the ozone treatment of atrazine. The order of reaction with respect to ozone is higher in raw water, because the organic substances, present in raw water expressed as TOC, consume additional ozone.

TABLE V. CIET mass concentrations (in  $\mu\text{g L}^{-1}$ ) dependence on ozone flow ( $Q$ ) in the model water sample at 22 °C during ozone treatment (a) and catalytic ozone treatment (b)

$t/\text{min}$	$Q / \text{L h}^{-1}$					
	15 <sup>(a)</sup>	55 <sup>(a)</sup>	105 <sup>(a)</sup>	15 <sup>(b)</sup>	55 <sup>(b)</sup>	105 <sup>(b)</sup>
0	0.15	0.15	0.15	0.15	0.15	0.15
5	0.10	0.10	0.13	0.07	0.07	0.11
10	0.05	0.07	0.09	0.03	0.06	0.07

TABLE VI. Determination of the order of reaction regarding atrazine decomposition ( $\gamma_0 = 0.15 \mu\text{g L}^{-1}$ ) at 22 °C in the model water samples using different ozone flow during ozone treatment (a) and catalytic ozone treatment (b)

Flow / $\text{L h}^{-1}$	15 <sup>(a)</sup>	55 <sup>(a)</sup>	105 <sup>(a)</sup>	15 <sup>(b)</sup>	55 <sup>(b)</sup>	105 <sup>(b)</sup>
$\ln k$	-2.208	-2.574	-2.974	-1.827	-2.390	-2.574
$\gamma_{O_3}/\text{mg L}^{-1}$	4.11	0.60	0.29	4.11	0.60	0.29
$\ln \gamma_{O_3}$	1.413	-0.511	-1.238	1.413	-0.511	-1.238
$n$	0.269			0.284		

### Atrazine Metabolites

As the model water with  $0.68 \mu\text{mol L}^{-1}$  CIET was treated by ozone, the by-products were formed.

Due to the method limitation, only CIET, CIAT and CEAT were analysed for studying the reactivity of the asymmetrically disubstituted atrazine. The ratio *N*-deethylation/*N*-de-*i*-propylation was 4 for ozone treatment and ozone treatment with a Pt-catalyst (Figures 3 to 5) showing no difference at the employed temperature. This value is lower than reported: 10 at  $\text{pH} = 3^5$  and 19 at  $\text{pH} = 7^7$  and higher than 3.5 at  $\text{pH} = 6^4$ . Such different values might be obtained due to the strong pH-dependent degradation of some intermediates.<sup>5</sup>

The degradation of atrazine over time was compared at different temperatures. The initial concentration of atrazine was  $0.68 \mu\text{mol L}^{-1}$ . The gas flow was kept constant at  $15 \text{ L h}^{-1}$ . At  $40 \text{ }^\circ\text{C}$  CIET decomposed after 5 min (Figure 3), at  $20 \text{ }^\circ\text{C}$  after 10 min (Figure 4), while at  $5 \text{ }^\circ\text{C}$

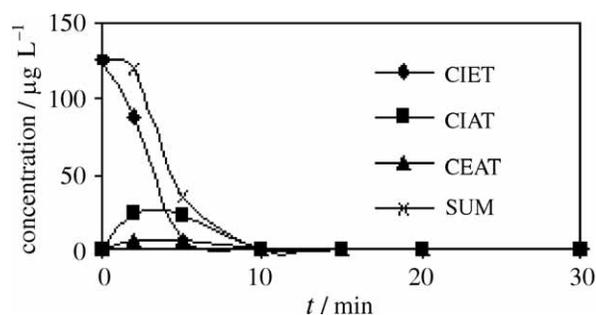


Figure 3. CIET decomposition at  $40 \text{ }^\circ\text{C}$ .

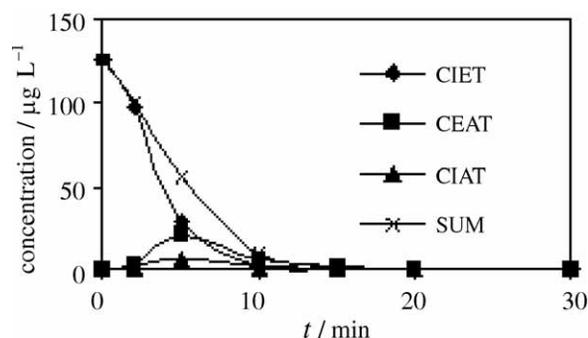


Figure 4. CIET decomposition at  $20 \text{ }^\circ\text{C}$ .

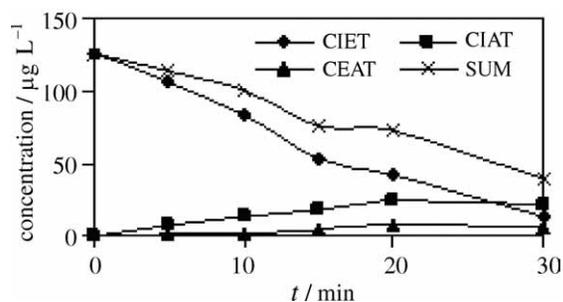


Figure 5. CIET decomposition at  $5 \text{ }^\circ\text{C}$ .

CIET was still present in the water sample after 30 min (Figure 5). The CIAT and CEAT contents reached the same high concentrations at all temperatures, but then dropped again over time. At higher temperatures, the curve peak was reached faster. The same situation was observed for catalytic ozone treatment.

When the drinking water with  $0.68 \mu\text{mol L}^{-1}$  CIET was treated by ozone CIAT was formed, but CEAT was not. The quantification limit for the GC method was probably the reason why CEAT was not found.

### Biodegradability vs. Time

The model water with  $4.6 \mu\text{mol L}^{-1}$  CIET was treated by ozone for 30 and 60 minutes at  $15 \text{ L h}^{-1}$ . The toxicity of atrazine found in literature data<sup>19</sup> to crustacean *Daphnia magna* was low. Atrazine is mainly toxic to plants, because it inhibits their photosynthetic capacity. The toxicity in water sample showed 20 % decrease after 1 hour of ozone treatment in comparison with the original drinking water sample.

The analyses of TN (Table VII) showed a drop of 2 %, and TOC dropped by 6 %. This could be connected to the reformation of CIET into cyanuric acid.<sup>20</sup>

The contents of Pt and Ti were measured in the water samples during ozone treatment experiments using Pt-catalyst. The Pt content rose from 0.02 to  $0.10 \mu\text{g L}^{-1}$  and Ti content from 0.06 to  $0.23 \mu\text{g L}^{-1}$  after 1 hour of ozone treatment. The changes in concentrations of both metals were negligible.

TABLE VII. The effect of CIET on TOC and TN values as well as toxicity during ozone treatment

Time of ozone treatment / min	TOC / $\text{mg L}^{-1}$	TN / $\text{mg L}^{-1}$	Toxicity / %
0	4.671	2.891	70
30	4.568	2.866	45
60	4.390	2.832	50

### CONCLUSIONS

The kinetics of atrazine decomposition in both the model and the drinking water samples was studied using ozone treatment and catalytic ozone treatment. We were determined that decomposition of atrazine followed the first order kinetics.

Two metabolites desethylatrazine and desisopropylatrazine were formed by the ozone treatment of atrazine, but the total sum of atrazine and both metabolites decreased over time. Experiments in model water did not show the effect of Pt-catalyst on atrazine degradation by ozone treatment (only 5.6 %), while in drinking water the constant rate rose by 27 %.

We have proved that Pt-catalyst increased the reaction rate of atrazine degradation by ozone treatment. *Daphnia magna* tests showed a 20 % decrease in the toxicity of drinking water treated by ozone with Pt-catalyst compared with the original drinking water sample.

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## SAŽETAK

### Kinetičko istraživanje katalitičkog ozoniranja atrazina

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Cilj ovog rada bio je istražiti raspad atrazina ozoniranjem uzoraka modelne i izvorne pitke vode korištenjem Pt-katalizatora, te određivanje učinkovitosti tog katalizatora. Konstante brzine raspada atrazina kataliziranim i nekataliziranim ozoniranjem su određene samo za uzorke modelne vode, a aktivacijska energija i red reakcije u odnosu na ozon su određeni za obje vrste uzoraka. Katalizirano ozoniranje utječe na raspad atrazina u uzorcima pitke vode. Tijekom ozoniranja praćene su koncentracije nekih metabolita u uzorcima modelne i pitke vode. Određena je toksičnost uzoraka originalne pitke i modelne vode na račiću *Daphnia magna*.